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Kinetics and Mechanism of Os(VIII)-Catalysed Oxidation of some Substituted trans-Cinnamic Acids by Chloramine-T in Alkaline Medium — A Non-Linear Hammett Plot

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Abstract: The kinetics and mechanism of Os(VIII) catalysed oxidation of some substituted trans-cinnamic acids by chloramine-T in presence of alkaline medium has been investigated. The order with respect to [CAT] is zero and is [OsO$_4$] one. The reaction is fractional order in [substrate]. The rate dependence on [OH$^-$] is inverse first order. Both the electron-releasing and withdrawing substituents facilitate the reaction rate. The observed rate constants for substituents are plotted against Hammett constant σ, a non-linear, 'V' shaped curve is obtained. The electron-withdrawing substituents fall on one side of the curve having a negative ρ value, and electron-releasing substituents fall on the otherside with positive ρ value. The break in the Hammett plot is due to change in the nature of transition state. The mechanism proposed and the derived rate law are in confirmity with the observed results.

The kinetics of Os(VIII)-catalysed oxidation of cinnamic acid by chlorate[1] and Ce(IV)[2] have already been reported. But there is no systematic kinetic report on the Os(VIII) catalysed oxidation of cinnamic acid by N-halocompounds. This promted as to undertake the title for investigation. Many oxidation reactions[3-6] are carried out using chloramine-T (CAT). The reaction has been studied under different experimental conditions, in the presence of sodium hydroxide using water as a solvent. The reaction does not take place in the absence of the catalyst. Osmium tetroxide is found to be catalysing the reaction.

EXPERIMENTAL

Reagents. All the cinnamic acids used were of Fluka sample. CAT, NaOH and OsO$_4$ were of AR grade. Kinetic runs were followed by estimating CAT by standard iodometric method. Doubly distilled water was employed second distillation being from alkaline permanganate solution in all glass assembly.

Kinetic measurements. For kinetic runs, a measured amount of CAB pre-equilibrated at 35°C was rapidly added to the thermally equilibrated mixture containing appropriate amounts of the cinnamic acid, alkali, osmium tetroxide and water. The progress of the reaction was monitored for two half lives by iodometric determination of unreacted CAB in a measured aliquot withdrawn at regular intervals of time. The zero order rate constants were reproductive within ±3%.

Stoichiometry and product analysis. The reaction mixture containing excess of CAB in the presence of Os(VIII) and sodium hydroxide were kept for 24 hr, under kinetic conditions. The estimation of unreacted CAB had indicated that two moles of CAB were used up by one mole of CA.

$$\text{Ph-CH=CH-CO}_2\text{H}+2\text{R-SO}_2\text{-NCl}^-\text{Na}^+ +2\text{H}_2\text{O} \xrightarrow[\text{Os(VIII)}]{\text{OH}^-} \text{PhCHO}+\text{OHCCO}_2\text{H}+2\text{RSO}_2\text{NH}_2 +2\text{NaCl} \qquad (1)$$

For identifying the product excess of oxidant was mixed with substrate under kinetic conditions. After the reaction was completed, the reaction mixture was neutralised with con HCl and then the products were extracted by ether. The organic layer was separated, dried and evaporated, a semi-solid was obtained and then analysed by Co-TLC method (silica-gel and the samples were spotted using $CHCl_3$ solvent). The spots of the products were developed in the CH_2Cl_2 and benzene (3:1 v/v) solvent mixture along with the spots of authentic samples of benzaldehyde and glyoxalic acid. After developing, the locations of the spots were identified using iodine vapour and their positions were compared. The two spots obtained for products was identical with benzaldehyde and glyoxalic acid.

RESULTS AND DISCUSSION

The reaction has been found to be zero order with respect to the disapperance of CAT as evidenced by a good linearity in the plot of titre vs time. The zero order rate constants (k_0 mol dm^3 s^{-1}) with respect to CAT are also constant over a wide range in [CAT] (Table 1).

Table 1. Zero Order Rate Constants (k_0) for different Concentration of Chloramine-T at 35°C

10^3[CAT] mol dm^{-3}	10^2 [CA] mol dm^{-3}	$10^3 k_0$ mol dm^{-3} sec^{-1}
0.25	1.15	7.41
0.50	1.15	7.22
0.75	1.15	7.27
1.00	1.15	7.35
1.25	1.15	7.14

[Os(VIII)] =5.0×10^{-5}mol dm^{-3}; [OH^-] = 5.5×10^{-3}mol dm^{-3}

The pseudo-zero order rate constants increase in increasing the substrate concentration (Table 2). The plot of logk_0 versus log[CA] for all the compounds studied have been found to be linear with slopes less than unity indicating fractional order dependence on [CA]. The double reciprocal plots of $1/k_0$ versus 1/[CA] are linear with finite intercepts on the inverse rate axis indicating complex is formed in the reaction. Without changing the conditions some important substituents are studied. All the substituents obeyed Michaelis-Menten type plot with respect to substrate. Hence the substituents follow the same mechanism (Table 3).

The effect of alkali has been studied by varying the concentration of OH^- at a given substrate concentration. Although the reaction rate is greatly affected by an increase in concentration of OH^-. The plot of $\log k_0$ versus $1/[OH^-]$ shows that the order with respect to $[OH^-]$ is inverse first order (Table 4).

Table 2. Zero Order Rate Constants (k_0) for different Concentration of Cinnamic acid at 35°C

10^3[CAT] mol dm^{-3}	10^2 [CA] mol dm^{-3}	$10^3 k_0$ mol dm^{-3} sec^{-1}
1.00	0.77	5.52
1.00	0.95	6.47
1.00	1.15	7.35
1.00	1.33	8.15
1.00	1.55	9.03
1.00	1.71	9.65

[Os(VIII)] $=5.0\times10^{-5}$ mol dm^{-3}; $[OH^-]$ = 5.5×10^{-3} mol dm^{-3}

Table 3. Effect of some Substituent Concentration on the Reaction rate at 35°C

	10^3 x k_0/mol dm^{-3} s^{-1} at 10^3 x [CA]/mol dm^{-3}			
Cinnamic acids [CA]	2.0	3.0	4.0	6.0
1 -H	2.18	2.91	3.55	4.69
2 p-NO_2	8.40	10.61	12.70	16.91
3 p-Cl	3.59	4.62	5.58	6.91
4 m-NO_2	7.19	9.38	11.64	15.92
5 p-CH_3	3.42	4.30	5.10	6.31
6 p-OCH_3	6.83	9.02	11.17	16.17
7 o-Cl	3.65	4.83	5.92	8.05
8 o-NO_2	9.24	12.22	15.18	21.26
9 o-OCH_3	10.66	14.07	17.58	24.79

[CAT]=1.00 x 10^{-3}mol dm^{-3}; [NaOH] = 5.5 x 10^{-3}mol dm^{-3}; $[OsO_4]$ = 5.0 x 10^{-5}mol dm^{-3}.

The reaction rate increases with increase in [Os(VIII)]. The plots of $\log k_0$ versus log[Os(VIII)] are linear with the slope of unity confirming first order dependence on [Os(VIII)] Table 5.

The rate data at different compositions of t-butanol (Table 5) shows that the rate increases with the polarity of the medium, indicating the possible formation of activated complex in the transition state, which is more hydrated than the reactants. Addition of sodium perchlorate to the reaction mixture does not alter the oxidation rate (Table 5) and hence no ion-ion (or) ion-dipole interaction in the slow-step.

The possibility of radical involvement in the reaction is ruled out as the addition of acrylonitrile in the reaction mixture developed no turbidity.

Table 4. Zero Order Rate Constant (k_o) for different Concentration of OH^- at 35°C

10^3 [OH^-] mol dm^{-3}	$10^3 k_0$ mol dm^{-3} sec^{-1}
5.50	7.28
7.65	5.89
12.75	3.28
20.00	2.01
25.50	1.74

[CA] = 1.15×10^{-2} M; [CAT] = 1.00×10^{-3} mol dm^{-3};[Os(VIII)] = 5.0×10^{-5} mol dm^{-3}

Table 5. Zero Order Rate Constants (k_o) for the Variation of Osmium tetroxide, t-butanol and Sodium perchlorate at 35°C

10^5[Os(VIII) mol dm^{-3}	% t-butanol mol dm^{-3}	10^3[$NaClO_4$] mol dm^{-3}	$10^3 k_0$ mol dm^{-3} sec^{-1}
2.5	-	-	3.19
5.0	-	-	7.35
7.5	-	-	10.50
10.0	-	-	14.47
12.5	-	-	18.31
5.0	0	-	7.35
5.0	5	-	6.92
5.0	10	-	6.10
5.0	15	-	5.71
5.0	20	-	4.73
5.0	25	-	4.19
5.0	-	1.0	7.31
5.0	-	2.0	7.35
5.0	-	3.0	7.27
5.0	-	4.0	7.30
5.0	-	5.0	7.20

[CAT] = 1.00×10^{-3} moldm^{-3}; [CA] = 1.15×10^{-2} moldm^{-3}

In order to investigate the effect of temperature on the reaction rate, the reaction have been carriedout at 30°, 35°, 40° and 45°C. The plots of $\ln(k_0/T)$ versus $1/T$ is found to be linear. The rate constant and thermodynamic parameters are tabulated in Table 6.

Mechanism and Rate Law. Chloramine- T act as a strong electrolyte in aqueous solution[7,8] and dissociate to give $RNCl^-$ (eq. 2)

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \qquad (2)$$

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad (3)$$

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \qquad (4)$$

$$RNHCl + H_2O \rightleftharpoons HOCl + RNH_2 \qquad (5)$$

$$HOCl \rightleftharpoons OCl^- + H^+ \qquad (6)$$

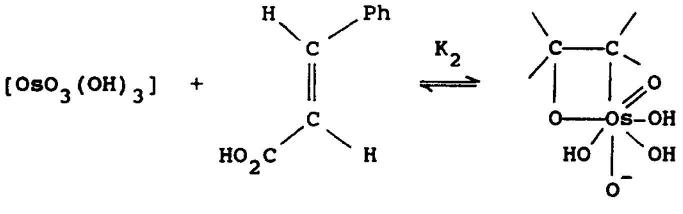
$$R = CH_3\text{-}C_6H_5\text{-}SO_2\text{-}$$

However, equilibria (3)-(6)[7,9,10,11] have been reported in acidic media. In view of the fact that the kinetic order with respect to [CAT] zero, the probable oxidising species can not be identified because the oxidant is involved in the fast step. But in basic medium, the probable oxidising species may be $RNCl^-$[12].

Osmium tetroxide turns a red $[OsO_4(OH)_2]^{2-}$ in strong alkaline solution[13]. However a dilute alkaline solution of OsO_4 converts $[OsO_4(OH)_2]^{2-}$ into $[OsO_3(OH)_3]^-$ in agreement with the results reported by Sauerbrum and Sandell[14]. Since the rate decreased with increasing $[OH^-]$ all the species subsequent to $[OsO_3(OH)_3]^-$ must be less reactive.

The above experimental observations viz, zero order with respect to [CAB] first order with respect to [Os(VIII)], fractional order in [CA], and inverse first order dependence on hydroxide ion concentration, a reaction mechanism comprising steps (7 to 12) can be suggested.

$$[OsO_3(OH)_3]^- + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [OsO_4(OH)_2]^{2-} + H_2O \qquad (7)$$



(C_1)

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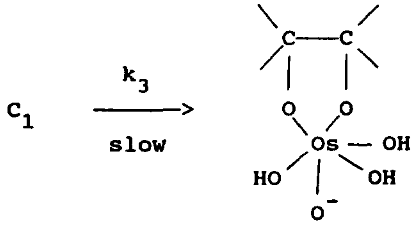

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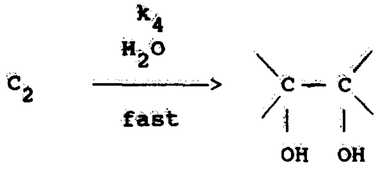

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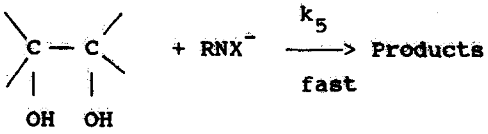

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$$Os(VI) + RNX^- \xrightarrow[\text{fast}]{k_6 \; H_2O} Os(VIII) + RNH_2 + HX \qquad (12)$$

The rate law can be derived as follows

$$\frac{-d[RNX]}{dt} = k_3C_1 \qquad (13)$$

$$= \frac{k_3K_2[CA][OsO_3(OH)_3^-]}{\{1 + K_2[CA]\}\ K_1[OH^-]}$$

$$k_{obs} = \frac{k_3K_2[CA][Os(VIII)]}{K_1[OH]+K_1K_2[CA][OH^-]} \qquad (14)$$

Effect of substituent on the reaction rate. As an extention of the present investigation, the kinetics of oxidation of some ortho-, meta- and para-substituted cinnamic acids with CAT is followed at four different temperatures (30-45°C). The zero order rate constants (k_0) and the thermodynamic parameters calculated using Eyring's equation are given in the Table 6.

The rate data are analysed from the linear free energy relationships. In the Table 6 the entropy of activation is not constant for all the substituents. One of the conditions necessary for the applicability of the linear free-energy relationship is the constancy of the entropy of activation[15]. However in most reaction series, this is not so[16,17]. If the Hammett equation is valid at one temperature, the condition for its validity at any other temperature is a linear relationship between ethalpies and entropies[18,19] and this is called the isokinetic relationship.

$$\Delta H^{\#} = \Delta H_0^{\#} + \beta \Delta S^{\#} \qquad (15)$$

Table 6. Thermodynamic Parameters for the Oxidation of Substituted Cinnamic acids by CAT in Presence of Oxalic acid Calculated from plots of In(k_0/T) versus 1/T

S.No.	Substituent	$k_0 \times 10^3$ (mol dm^{-3} s^{-1})				$H^{\#}$ (kJmol^{-1})	$-S^{\#}$ (JK^{-1}mol^{-1})	r	sd
		30°	35°	40°	45°				
1	- H	2.16	2.91	3.63	4.85	39.9	164.6	0.998	0.023
2	p-CH_3	2.92	4.30	6.14	8.85	56.5	107.4	0.999	0.006
3	p-OCH_3	6.59	8.85	12.50	19.36	57.8	106.4	0.994	0.056
4	o-CH_3	3.50	5.07	7.07	10.40	55.1	110.4	0.999	0.019
5	o-OCH_3	8.87	14.15	20.35	32.75	66.0	66.5	0.998	0.036
6	p-NO_2	8.13	10.65	13.13	16.58	35.1	169.4	0.999	0.015
7	p-Cl	3.49	4.62	5.58	6.69	31.8	187.1	0.994	0.033
8	p-Br	3.80	4.68	5.29	6.90	28.0	199.0	0.987	0.041
9	p-F	2.77	3.58	4.10	5.28	30.6	193.1	0.998	0.037
10	m-NO_2	8.12	9.37	11.46	12.74	22.3	211.5	0.994	0.026
11	m-Cl	3.95	4.57	5.21	6.11	20.5	223.6	0.998	0.010
12	m-F	3.79	4.77	5.74	6.94	29.5	194.1	0.999	0.015
13	o-NO_2	10.00	12.21	14.15	17.22	25.9	197.9	0.998	0.016
14	o-Cl	3.96	4.77	5.59	6.82	26.1	205.1	0.998	0.013
15	o-Br	2.98	3.87	4.70	6.12	35.1	177.6	0.997	0.022

A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ gives a straight line with correlation co-efficient (r=0.996). The isokinetic temperature(ß) obtained from the slope is 299K. The good correlation co-efficient implies that the reaction with all the substituted cinnamic acids follow the same common mechanism.

However Exner[20,21] criticised the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities depend on each other. When measurements at two temperatures have been made, the experimental data can be treated by the following equation[22,23]

$$\log k_{2(T_1)} = a + b \log k_{2(T_2)}$$

Where $T_2 > T_1$

A good correlation (r = 0.909) is obtained when $\log k_{(45°)}$ is plotted against $\log k_{(30°)}$ shows that the reaction under investigation follow the same common mechanism.

Deviation from the Hammett Relationship. Hammett equation applied with the usual substituent constant σ and k_{obs} data of ortho-, meta- and para-substituted cinnamic acids exhibit a 'V' shaped curve (Fig. 1). This similar type of 'V' shaped curve in Hammett plot has been observed earlier[24,25,26] in some reaction series.

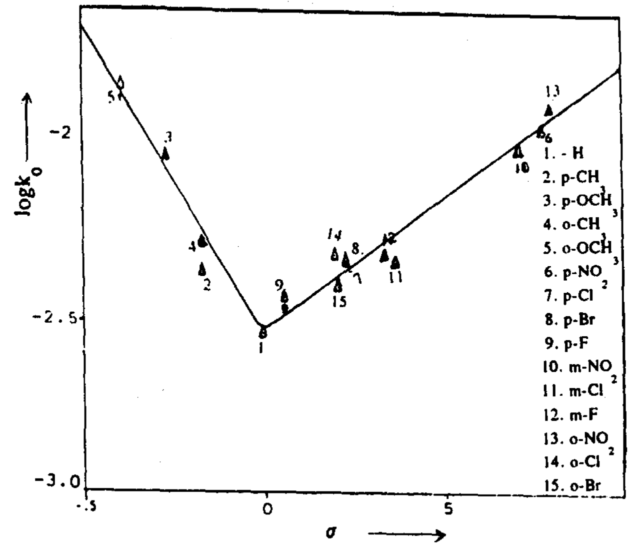


Fig. 1. Hammett plot for oxidation of some substituted trans-cinnamic acids by chloramine-T

The electron releasing substituents fall on the one side of the curve with a negative slope and the electron-withdrawing substituents on the other side with a positive slope. The values of ρ_+ and ρ_- at different temperature are given in Table 7.

Table 7. The Reaction Constant for Oxidation of Substituted Cinnamic acids by Chloramine-T

Temperature °C	ρ_+	ρ_-
30	0.74	1.72
35	0.71	1.83
40	0.71	1.98
45	0.66	2.19

The reason for the break in the Hammett plot is

1. A change in the reaction mechanism
2. A change in the rate-determining step with change in the nature of the substituents.
3. A change in the transition state.

In this reaction, the non-linear Hammett plot is not due to the change in the reaction mechanism with respect to substituents, because the isokinetic plot ($\Delta H^{\#}$ versus $\Delta S^{\#}$) and Exner plot give a good correlation. Some important substrates (substituent) follow Michaelis-Menten's plot and yield defenite intercept (Fig. 2). So the non-linear Hammett plot due to the nature of the substituent is also ruled out. Finally, the observed non-linear plot in the logk$_0$ versus σ is only due to the change in the transition state.

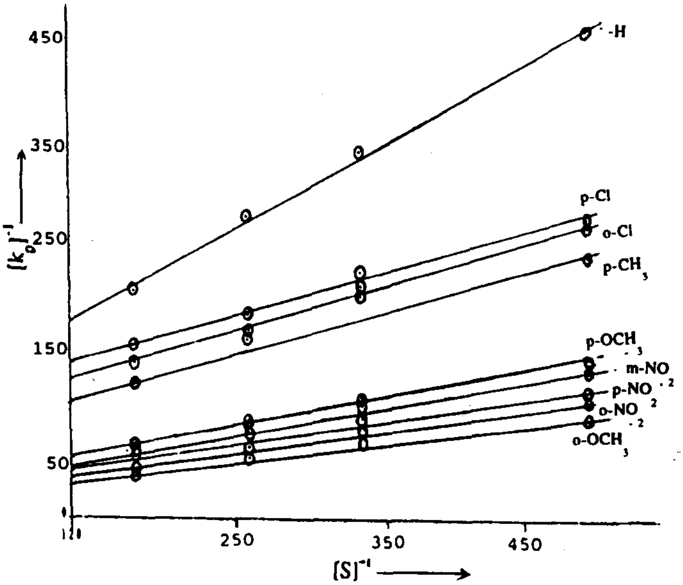
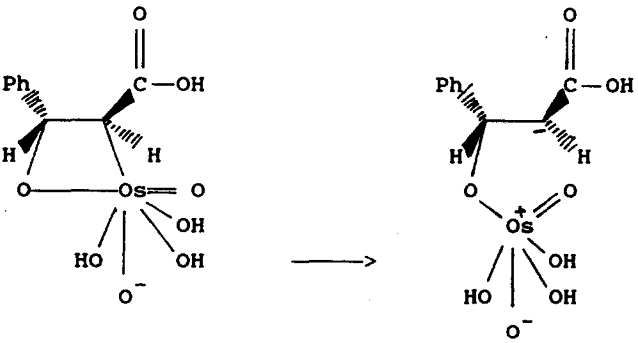


Fig. 2. Michaelis-Menten plot for oxidation of some substituted trans-cinnamic acids by Chloramine-T

Based on the above experimental observations we assume a complex formation by an interaction of the substrate and Os(VIII) (eq.8). The unsubstituted CA is least reactive in this series. But both the electron-releasing and withdrawing substituents facilitate the rate of the oxidation considerably. The electron attractors accelerate the reaction rate only when the rate-determining step proceeds with the development of negative charge on the α or ß carbon (eq. 17) in cinnamic acid.



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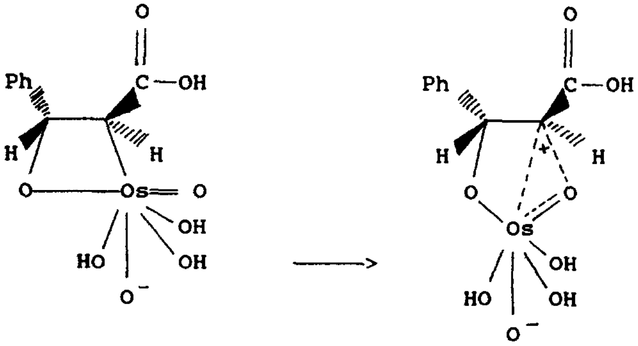
Same type of transition state has been observed by Lee and Benito[27].

The electron-releasing substituent requires a carbonium ion in the transition state to accelerate the rate of the reaction. The development of positive charge is as shown in (eq.18).



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